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ELECTRON PARAMAGNETIC RESONANCE OF V^{4+} IONS IN LANTHANUM-ALUMINOSILICATE GLASSES

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The EPR and optical absorption spectra of V^{4+} ions and their relation with the structural features of glasses in the system $La_2O_3 – Al_2O_3 – SiO_2$ are investigated. Three characteristic ranges of the V^{4+} EPR parameters are established: I) $A_\parallel \approx 167 \times 10^{-4}$ cm^{-1}, $g_\parallel = 1.937 – 1.938$; II) $A_\parallel \approx (163 – 164) \times 10^{-4}$ cm^{-1}, $g_\parallel = 1.939 – 1.940$; III) $A_\parallel \approx (156 – 159) \times 10^{-4}$ cm^{-1}, $g_\parallel = 1.945$. It is shown that in the region I with low La_2O_3 content the lanthanum is predominately a modifying ion, and in glass with a high La_2O_3 concentration lanthanum gradually occupies a site in the glass, bonding silicon-oxygen and aluminum-oxygen tetrahedra, i.e., it becomes a glass former even though its ionic radius is large. Region III glasses with high La_2O_3 content possess a high softening temperature and anomalously high thermal conductivity (about 12.6 W/(m · K)).

Key words: electron paramagnetic resonance (EPR), optical spectra, lanthanum-aluminosilicate glass, vanadium (IV) ions.

In the present work we studied the system $La_2O_3 – Al_2O_3 – SiO_2$ in connection with the development of thermally stable glasses with low CLTEs $(35 – 50) \times 10^{-7}$ K^{-1} and a prescribed narrow transmission band in the green part of the spectrum (peaking near 500 nm) for signal lights used in aircraft.

Some properties of the glasses in this system have been investigated in [1]. These glasses are characterized by a high refractive index (up to 1.767) and high density (up to 4.17 g/cm^3). The main distinguishing feature of these glasses is their high deformation-onset temperature (855 – 940°C) with CLTE $(33.7 – 64.0) \times 10^{-7}$ K^{-1}. As compared with other commercial tungsten-group glasses with CLTE about 40×10^{-7} K^{-1}, the deformation-onset temperature of lanthanum-aluminosilicate glasses is shifted by 80 – 100°C toward high temperatures, i.e., they can be used for work at higher temperatures (750 – 800°C). Possessing anomalously high thermal conductivity (about 12.6 W/(m · K)), these glasses find applications as integrated-circuit boards with fast heat removal and as laser materials.

The investigation of the system $La_2O_3 – Al_2O_3 – SiO_2$ is also of fundamental value. The glass-formation region in this system at the maximum synthesis temperature 1600°C was determined in [2]. The region of glass-formation becomes wider when $La_2O_3 – Al_2O_3 – SiO_2$ glasses are synthesized by the method of microwave fusion in a sold container at approximate temperature 2000°C in air [1]. The products of crystallization of glasses in this system have been studied in [3 – 5] in different sections of the glass-formation region. It was determined that for high La_2O_3 content lanthanum disilicate forms and for comparatively low content lanthanum-aluminosilicate $La_4Al_4Si_5O_{22}$ forms.

It has been suggested in [1] on the basis of an analysis of the properties of $La_2O_3 – Al_2O_3 – SiO_2$ glasses with different $La_2O_3 : Al_2O_3$ ratio but constant SiO_2 content that the La^{3+} ions in the structural network of glasses in this system can occupy two non-equivalent positions, becoming incorporated in the silicon-oxygen part of the structure with a Si – O – La bond being formed or replacing the Al^{3+} ions in the aluminum-oxygen groups.

In the present work we investigated the electron paramagnetic resonance (EPR) and optical absorption of V^{4+} ions and their relation with the structural particularities of the glasses in the entire range of glass formation in the system $La_2O_3 – Al_2O_3 – SiO_2$. As a method for studying the structure of glass, Cu^{2+} and V^{4+} EPR has been used in many works, for example, [6].

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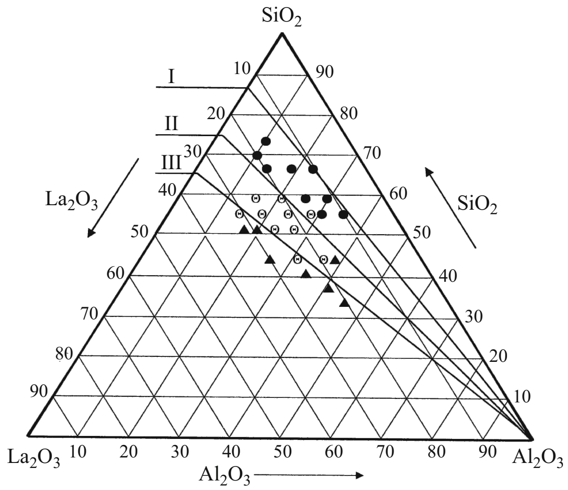

Fig. 1. $La_2O_3 – Al_2O_3 – SiO_3$ glasses studied: ● (region I), ▲ (region II), Θ (region III)) compositions for which spectra with one of three sets of spectral parameters are observed.

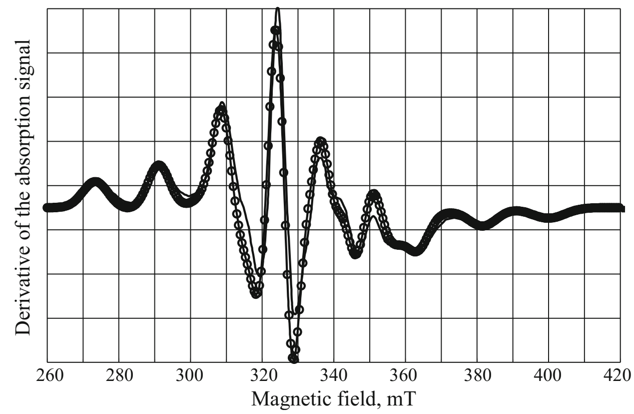

Fig. 2. EPR spectrum of V^{4+} in glass with the composition 20 La_2O_3, 20 Al_2O_3, 60 SiO_2 (molar content, %): solid curve) experimental spectrum; ○) model spectrum.

The glasses in the system $La_2O_3 – Al_2O_3 – SiO_2$ were synthesized in an electric furnace at the maximum temperature 1600°C. The samples were annealed at 750 – 850°C. The experimental glass compositions are plotted on a Gibbs triangle (Fig. 1). Because the soaking time of the melt was long the glass-formation region was wider than in [2] for the same temperatures.

The EPR spectra were investigated for all compositions indicated in Fig. 1. The measurements were performed with a modified RÉ-1306 3-cm range radiospectrometer. Samples containing an admixture of V^{4+} ions or Cu^{2+} ions as structure indicators were studied first. It was determined that the EPR spectra of the V^{4+} ions are more sensitive to a change of the composition of the glass in this system than those of the Cu^{2+} ions. As result, the V^{4+} ions were used to study the structure of the glass.

A PC with a computer program which we devised was used to process the experimental spectra and determine the EPR parameters of V^{4+} [7]. The parameters of the EPR spectra of V^{4+} $g_\perp$, $g_\|$, $A_\perp$, and $A_\|$ were determined; a complete set characterized the nearest-neighbor environment of a V^{4+} ion and therefore the structure of the glass [6]. As an example, we display in Fig. 2 the experimental EPR spectrum of V^{4+} in the lanthanum-aluminosilicate glass and a model spectrum calculated for the following parameters: $g_\| = 1.937$, $g_\perp = 1.967$, $A_\| = 163.4 \times 10^{-4}$ cm^{-1}, and $A_\perp = 54 \times 10^{-4}$ cm^{-1}.

The optical absorption spectra of samples of vanadium-containing glass in the system $La_2O_3 – Al_2O_3 – SiO_2$ were also measured. In addition, the optical spectra of other transition elements were studied in connection with obtaining a narrow transmission band in the green part. The spectra were recorded with a standard SF-8 spectrophotometer in the wavelength range 300 – 1200 nm at room temperature.

The composition of the glasses, the EPR spectral parameters of V^{4+}, and the position of the optical absorption bands are presented in Table 1.

Three regions of values of the EPR spectral parameters of V^{4+} ions are characteristic for the experimental composition of the system:

I) $A_\| \approx 167 \times 10^{-4}$ cm^{-1}, $g_\| = 1.937 – 1.938$;
II) $A_\| \approx (163 – 164) \times 10^{-4}$ cm^{-1}, $g_\| = 1.939 – 1.940$;
III) $A_\| \approx (156 – 159) \times 10^{-4}$ cm^{-1}, $g_\| = 1.945$.

It is evident from Fig. 1 that each set of EPR parameters corresponds to a definite composition range. For the experimental glasses, an abrupt change of the spectral parameters at a transition from one composition region to another is characteristic. This is due to the fact that because of the double covalent bond with one of the oxygen atoms the vanadyl complex (Fig. 3) is very stable and reacts only weakly to a change of the chemical bonds with equatorial ligands. Ordi-

TABLE 1.

Composition	Molar content in the glass, %			$g_\|$	$A_\| \times 10^4$ cm^{-1}	$g_\perp$	$A_\perp \times 10^4$ cm^{-1}	ΔE_1, cm^{-1}	ΔE_2, cm^{-1}
	SiO_2	Al_2O_3	La_2O_3						
1	65	25	10	1.938	166.9	1.99	61.1	15,870	–
2	60	20	20	1.939	163.4	1.98	58.3	15,870	–
3	55	20	25	1.936	163.2	1.98	58.3	15,870	10,520
4	55	15	30	1.946	156.6	1.98	57.9	15,870	10,000
5	50	20	30	1.940	159.9	1.98	57.6	15,870	10,000

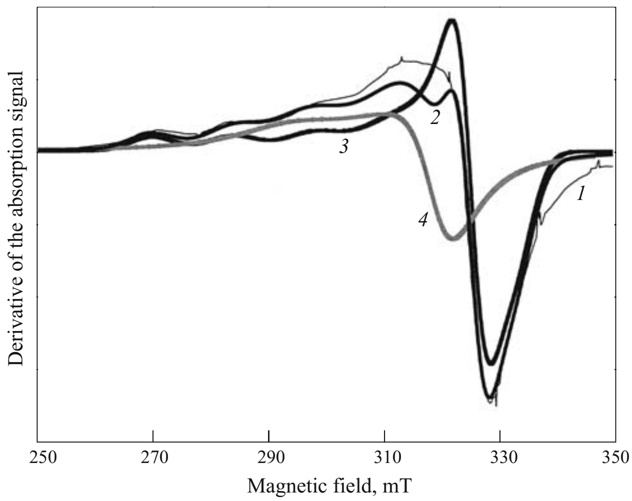

Fig. 3. EPR spectrum of Cu^{2+} in a sample treated at temperature 700°C: *1*, *2*) experimental and computational spectra, respectively; *3*, *4*) components of the computed spectrum.

narily, in oxide glasses the V^{4+} ion is present in the form of the vanadyl ion VO^{2+} with one shortened bond in the axial position.

An appreciable reaction occurs only for substantial changes in the nearest-neighbor environment of the vanadyl ion; as a rule, such changes occur in the glass-forming part of the glass. Ordinarily, these changes are manifested as an abrupt change of the spectral parameters.

The optical absorption spectrum characteristic for certain glasses of the system considered here is shown in Fig. 4. Two absorption bands can be seen; their positions are presented in Table 1. However, in most of the glasses studied only one absorption band is observed — in the region 630 – 640 nm, while the other and much weaker band is not observed in the optical spectrum. The ultraviolet absorption edge in the glasses of this system is mainly due to a charge-transfer transition of ions in the valence form V^{5+}, in which vanadium is predominately present in these glasses.

Apparently, in the system $La_2O_3 – Al_2O_3 – SiO_2$ the fraction of V^{4+} ions to which is ascribed the electronic absorption

TABLE 2.

Composition	Molar content in the glass, %			$g_\parallel$	$A_\parallel \times 10^4$ cm^{-1}	Published source
	Na_2O	SiO_2	La_2O_3			
6	20	80	–	1.935	172.0	[8]
7	25	75	–	1.938	170.3	[8]
8	30	70	–	1.939	169.0	[8, 9]
9	25	70	5	1.937	169.9	*
10	20	70	10	1.940	168.3	*
11	17.5	70	12.5	1.940	168.9	*

* Data obtained in the present work.

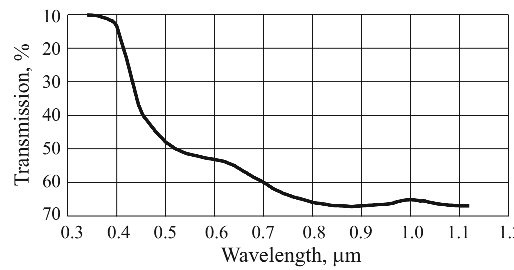

Fig. 4. Typical optical absorption spectrum of vanadium-containing glasses of the system $La_2O_3 – Al_2O_3 – SiO_2$.

band in region 630 – 640 nm is small, which is why the optical spectrum as a whole and the band ΔE_2 (10,000 cm^{-1}) in particular are weak.

Since the EPR of V^{4+} ions in $La_2O_3 – Al_2O_3 – SiO_2$ glasses has not been studied before, in order to make comparisons with other systems we studied the EPR spectrum of V^{4+} in simple glassy systems where equimolecular substitution of La_2O_3 for one or another component is made. The binary sodium – silicate glasses, for which the EPR spectra of V^{4+} have already been studied in [8], were chosen for such a control system.

The spectral parameters obtained for the binary glasses of the system $Na_2O – SiO_2$ as well as the spectral parameters for the V^{4+} ion, found from the EPR spectra of V^{4+} for $Na_2O – La_2O_3 – SiO_2$ glasses obtained by equimolecular substitution of La_2O_3 for Na_2O with constant SiO_2 content (70%[4]), are presented in Table 2. It follows from [8] that the EPR spectra in silicate glasses are insensitive to the content and nature of the modifier. This is also evident from the data in Table 2 for binary sodium – silicate glasses. It also follows from Table 2 that the spectral parameters $A_\parallel$ and $g_\parallel$ in glasses with La_2O_3 content from 5 to 12.5% vary little as compared with the initial sodium-silicate glass with the composition 30% Na_2O and 70% SiO_2.

The substitution of Al_2O_3 for Na_2O in the system $Na_2O – La_2O_3 – SiO_2$ with constant La_2O_3 content equal to 10% engenders a smooth change of the spectral parameters, expressed as a weak decrease of $A_\parallel$ and $g_\parallel$ from values for the composition 10 (see Table 2) to values for composition 1 (see Table 1). The modifying ions compensate the negative charge in such a tetrahedron. Therefore, in the region I lanthanum acts predominately as a modifying ion.

Using the linear relation $g_\parallel = f(R_2)$ established in [10] the values of $g_\parallel$ characteristic for each of the three ranges of the spectral parameters were used to estimate the interionic distances V – O (R_2) in the vanadyl ion complex (see Fig. 3). In this work Hecht and Johnston showed that $g_\parallel$ depends only on R_2 — the distance between vanadium in the vanadyl complex VO^{2+} and the oxygen ligands in the equatorial plane, while $g_\perp$ depends only on R_1 — the distance to the vanadyl oxygen.

[4] Here and below, the molar content unless otherwise stipulated.

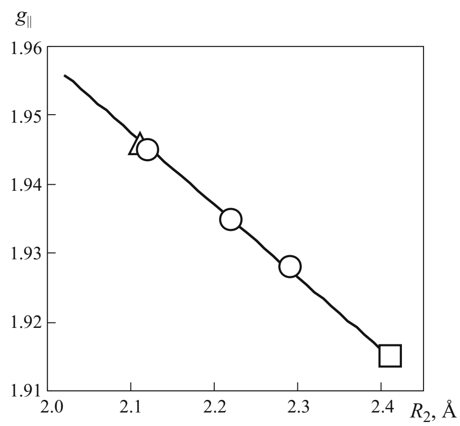

Fig. 5. $g_{\parallel}$ versus R_2 in oxide glasses: Δ) $La_2O_3 - Al_2O_3 - SiO_2$; □) $Al_2O_3 - P_2O_5 - M_2O_3$ (MO_2); ○) data of [10].

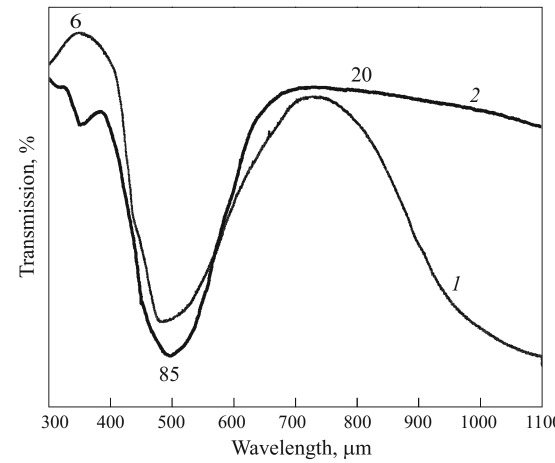

Fig. 6. Transmission spectra of glasses in the system $La_2O_3 - Al_2O_3 - SiO_2$ with 1 wt.% admixture of WO_3 (*1*) and 1 wt.% admixture of MoO_3 (*2*).

This linear dependence, which we constructed from the data in [10] (Fig. 5), is described by the equation

$$g_{\parallel} = 2.174 - 0.107R_2.$$

The dependence of the parameters of the EPR spectrum of VO^{2+} on the type of glass former is due to the fact that the values of these parameters are determined by the character of the chemical bonds in and the symmetry of the complex and by the interionic distances, which in turn are related with the structure of the glass-forming framework. The appearance of the new structural elements in the glass-forming framework is accompanied by substantial changes of the EPR parameters of VO^{2+}. This signifies that the complex VO^{2+} is subject to distortions imposed by the nature of the structural elements of the glass-forming framework. A strict calculation of the character of the deformation of the complex cannot be performed.

The values of $g_{\parallel}$ characteristic for each of the three ranges of the spectral parameters in the system $La_2O_3 - Al_2O_3 - SiO_2$ were used to evaluate the interionic distance $V - O$ (R_2) using the relation presented in Fig. 5. Evidently, $R_2 = 2.20$ Å for glasses whose parameters correspond to the region I, $R_2 = 2.17$ Å for region II, and $R_2 = 2.13$ Å for region III, i.e., as the La_2O_3 concentration increases and the SiO_2 concentration decreases in the glass the distance between the central ion of the vanadyl complex and the equatorial ligands becomes progressively shorter.

Comparing the system studied here $La_2O_3 - Al_2O_3 - SiO_2$ with the control systems $Na_2O - SiO_2$, $Na_2O - La_2O_3 - SiO_2$, and $Na_2O - SiO_2 - Al_2O_3 - La_2O_3$ showed that the V^{4+} EPR parameters change very little with equimolecular substitution of La_2O_3 for Na_2O and Al_2O_3 for Na_2O in the composition range with high SiO_2 content and comparatively low La_2O_3 content (≤ 12.5%). In the system $La_2O_3 - Al_2O_3 - SiO_2$ the region I of the EPR spectral parameters of V^{4+} corresponds to these compositions. For this reason, it can be supposed that in the region I the V^{4+} ions are found in an environment which is common for silicate glasses with composition close to the disilicate composition, in which the silicon ions act as glass-forming ions. In this case, lanthanum acts as a modifying ion.

On switching to region II and especially to region III the surrounding environment of the V^{4+} ions changes substantially because of changes in the structure of the glass. Our results can be interpreted assuming that in glasses with relatively low SiO_2 content and high La_2O_3 concentration the lanthanum gradually occupies sites in the glass network, binding the silicon-oxygen and aluminosilicate tetrahedra. Thus, it changes from being a modifier (for low concentrations of La_2O_3) to a glass former, though a very atypical one, since in contrast to ordinary glass formers its ionic radius is large.

It follows from the values of R_2 which we have obtained for glasses in the composition range studied in this work that the surrounding environment of V^{4+} ions seeks a more regular octahedral environment.

A high content of Al_2O_3 and La_2O_3 in silicate glass is accompanied by high thermal and chemical stability of hard glass and by low CLTE. This enabled us to used glass in this system as a base for obtaining green glasses for signal lights used in aircraft. As follows from Fig. 4, the transmission band of vanadium-containing glasses in the system $La_2O_3 - Al_2O_3 - SiO_2$ lies in the green part of the optical spectrum with a maximum near 550 nm.

The EPR and optical spectra of glasses with admixtures of elements in the first transition row as well as with Mo and W were studied. It was determined that of the elements in the first transition row Ti, V, Cr, and Cu can be present in the glasses, studied here, in valence states which give transmission in the blue and green parts of the optical spectrum and can be used as a base for developing light filters in the green range. An attempt to use different combinations of these elements did not give the desired result. The transmission band of W-containing glass, having a light blue color, lies in the

range 430 – 470 nm. The spectra of Mo-containing glasses are difficult to interpret because of the simultaneous presence of different valence forms of Mo. The transmission band in light-blue molybdenum glasses lies at 480 nm. It can be seen in Fig. 6 (curve *2*).

In summary, it has been found that glass with CLTE $44.2 \times 10^{-7}\ K^{-1}$, deformation-onset temperature 810°C, and transmission band peaking at 500 nm, i.e., satisfying all requirements for glasses used as green signal lights in aircraft, can be obtained on the basis of the system $La_2O_3 - Al_2O_3 - SiO_2$.

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